RATE CONSTANTS FOR THE REACTIONS OF OH WITH HFC- 134a (CF_3CH_2F) AND HFC- 134 (CHF_2CHF_2)

W. B. DeMore

Jet Propulsion Laboratory, California Institute of Technology

Abstract. Rate constants for the reactions of OH with HFC- 134a (CF_3CH_2F) have been measured relative to CH_3CCl_3, CH4 and HFC-125 (CF_3CHF_2). Rate constants for HFC- 134 (CF_2HCF_2H) were measured relative to CH_3CCl_3, HFC-1 25, and HFC- 134a, The measurements were made in a slow-flow, temperature controlled photochemical reactor, and were based on relative rates of disappearance of the parent compounds as measured by FTIR spectroscopy. The temperature range was 298-358 K. Hydroxyl radicals were generated by 254 nm photolysis of 03 in the presence of water vapor. Using current NASA/JPL rate constants for the reference compounds, temperature dependent rate constants of both compounds were derived. Rate constants obtained from the different reference compounds are in excellent agreement. The presently recommended rate constant for HFC- 134a [JPL 92-20, 1992; IUPAC, 1992] is too high by about 25%.

Introduction

At the present time there is interest in predicting the atmospheric lifetimes of compounds such as HFC-1 34a and HFC- 134, which may be used as substitutes for chlorine-containing CFCS in some refrigeration systems. Most saturated organic compounds containing a C-H bond are removed from the atmosphere mainly by H-atom abstraction by the hydroxyl radical, OH. Thus, to calculate the atmospheric lifetimes it is necessary to know the absolute values and temperature dependence of the rate constants for the abstraction reactions, as well as the atmospheric concentrations of OH. Measurements of rate constants relative to that for CH_3CCl_3 are especially useful, because global distributions of the latter, combined with the known emission rates [Midgely, 1989], have been used to calculate the CH_3CCl_3 lifetime in the atmosphere. Therefore, atmospheric lifetimes relative to that of methyl chloroform

Figure 1 shows 298 K data plotted according to Equation I for HFC- 134a and HFC- 134, both with reference to CH_3CCl_3. The ratio of slopes is 1.5, which indicates that the reaction ofHFC-134 with OH is 1.5 times faster than that of HFC-1 34a. at 298 K.

Six rate constant ratios and their temperature dependence were measured: $k(CH_3CCl_3)/k(134a)$, $k(CH_4)/k(134a)$, $k(125)/k(134a)$, $k(CH_3CCl_3)/k(134)$, $k(134)/k(134a)$, and $k(134)/k(125)$ The results for all ratios measured are shown in Arrhenius form in Figure 2(a-f).

Table 1 summarizes all the ratios measured, in Arrhenius form, as derived from linear least squares fits of the data shown in Figure 2. Table 2 lists the calculated rate constants for HFC- 134a, based on the three reference compounds used. Table 3 shows the resulting rate constants forHFC-1 34.

Some consistency checks may be noted in Table 1. The ratio $k(134)/k(134a)$, when calculated from the ratios of each HFC versus CH_3CCl_3, is 1.48 at 298 K, compared to the directly measured value 1.53. Similarly, the same ratio obtained from the HFC- 125 ratios is 1.51. The temperature dependences and A-factor ratios are slightly different, due to experimental error, but all indicate a higher E/R for HFC-134a compared to HFC-1 34.

The previously measured ratio $k(CH_3CCl_3)/k(CH_4)$ [DeMore, 1992b] can also be compared with the value calculated from the data of Table 1, using the ratios for CH_3CCl_3 and CH4 versus HFC-1 34a. The result is 0.54 exp(301 /T), compared to the directly measured value of 0.62 exp(291 /T).

Discussion

The derived rate constants for both HFC-1 34a and HFC-134 (Tables 2 and 3) from the different reference compounds are in remarkably good agreement, This implies that the rate constant data used for the reference compounds are self-consistent, It seems clear, however, that the presently recommended rate constant for HFC- 134a in JPL 92-20 and IUPAC [1992] is high by about 25%, from the standpoint of consistency with the reference compounds, Both the JPL 92-20 and the IUPAC recommendations for HFC- 134a are based on recent and extensive absolute measurements of the rate constant for this reaction, All studies report higher rate constants for HFC- 134a than would be consistent with the present work, although the actual data points of Gierczak et al., [199 1] near 298 K are only about 12% higher than those of the present work. The reason for higher results in other studies is not known, although absolute rate measurements for OH reactions sometimes give high values as a result of impurity effects, secondary reactions, or wall losses. [Clyne and Holt, 1979; Vaghjiani and Ravishankara, 1991; Wayne et al, 1992].

The present results for HFC- 134a imply that the atmospheric lifetime is 25°A longer than would be calculated from presently recommended rate constants [JPL 92-20, 1992; IUPAC, 1992] Based on the ratio $k(CH_3CCl_3)/k(134a)$ from the present work (Table 1), the lifetime of HFC-1 34a with respect to OH loss is 2.7 times longer than that of CH_3CCl_3 at an average atmospheric temperature of 277 K.

The previous database for HFC-134 is limited to the work of Clyne and Holt [1979] who obtained the rate constant expression $k = 2.8 \times 10^{-12} \exp(-1800/T)$ for the temperature range 294-434 K. This corresponds to a k(298 K) value which is about 17°/0 higher than that of the present work. The JPL 92-20 recommendation, $8.7 \times 10^{-13} \exp(-1500/T)$ is based only on the Clyne and Holt data at 294 K ($k = 5.3 \times 10^{-15}$ cm^3/molec-s.), with the temperature dependence being an estimate. From this expression, k(298 K) = 5.7×10^{-15} Thus the JPL 92-20 recommendation agrees with the present work at 298 K.

Based on the three rate constants obtained in the present work for both HFC- 134a and HFC- 134 (Tables 2 and 3), the following expressions are recommended:

$$k(134a) = 1.3 \times 10^{-12} \exp(-1740/T)$$
$$k(298\ K) = 3.8 \times 10^{-15}\ cm^3/molec\text{-}s$$

$$k(134) = 1{,}6 \times 10^{-12} \exp(-1680/T)$$
$$k(298\ K) = 5.7 \times 10^{-15}\ cm^3/molec\text{-}s$$

These were obtained by averaging the Arrhenius parameters in Tables 2 and 3, respectively. They are consistent with the directly measured ratio k(134)/k(134a) (Table 1). The absolute uncertainty for both rate constants at 298 K is probably 10% or less, considering the excellent agreement from different reference compounds. The uncertainties in the E/R values are about ± 150 K.

In general the A-factor ratios of Table 1 are approximately equal to the ratios of the number of hydrogen atoms in the respective compounds. For example, the ratio 0.48, which was obtained for both A(125)/A(l 34) and A(125)/A(134a), is close to the statistical value of 0.5, This implies that, at least for similar structures, the A-factor is proportional to the number of hydrogen atoms This suggestion has been made previously [Jolly et al., 1985]. The most severe departure from this rule in the present data is the ratio $A(CH_3CCl_3)/A(134)$, which is 0.84 (Table 1) rather than the hypothetical 1.5. It is not clear whether this is a true exception to the rule or the result of experimental error in the ratio measurement. The corresponding ratio for 134a, 1.22, is closer to the statistical value.

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References

Clyne, M. A. A., P. M. Holt, Reaction Kinetics Involving Ground and Excited Hydroxyl Radicals, Part 2. Rate Constants for Reactions of OH with Halogenomethanes and Halogenoethanes, J. Chem. Sot. Faraday Trans. 2, 75, 582, 1979,

DeMore, W. B., Rates of Hydroxyl Reactions with some HFCS, Optical Methods in Atmospheric Chemistry, 1715X 72-76, 1992a.

DeMore, W. B., Relative Rate Constants for the Reactions of OH with Methane and Methyl Chloroform, Geophys. Res. Lett., 19, 1367-1370, 1992b.

Gierczak, T., R. Talukdar, G. L. Vaghjiani, E. R. Lovejoy, and A. R. Ravishankara, Atmospheric Fate of Hydrofluoroethanes and Hydrofluorochloroethanes: 1. Rate Coefficients for Reactions with OH, J. Geophys. Res. 96, 5001, 1991.

IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, Evaluated Kinetic and

Photochemical Data for Atmospheric Chemistry Supp. IV, J. Phys. Chem. Ref. Data, 21, No. 6, 1125-1568, 1992.

Jolly, G. S., G. Paraskevopolous, and D. L. Singleton, Rates of OH Radical Reactions. XII, Int. J Chem Kinet., 17, 1-10, 1985.

JPL 92-20, Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Publication 92-20, Jet Propulsion Laboratory, California Institute of Technology, 1992.

Midgely, P. M., The production and release to the environment of 1,1,1 trichloroethane (methyl chloroform), Atmos. Environment, 23,2663-2665, 1989.

Prather, M., and C. M. Spivakovsky, Tropospheric OH and the lifetimes of hydrochlorofluorocarbons, J. Geophys. Res., 95, 18723-18729, 1990.

Vaghjiani, G. L., and A, R. Ravishankara, New measurement of the rate coefficient for the reaction of OH with methane, Nature, 350,406-409, 1991.

Wayne, R, P., C. E. Canosa-Mas, A. C. Heard, and A. D. Parr, On Discrepancies Between Different Laboratory Measurements of Kinetic Parameters for the Reaction of Hydroxyl Radical with Halocarbons, Atmospheric Environment. 26A, 2371-2379, 1992.

DeMore: Rate Constants for HFC-1 34a andllFC-134

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Figure 1. Depletion factors at 298 K for HFC-1 34a and HFC- 134 versus those for CH_3CCl_3 as the reference compound, plotted according to Equation I.

Figure 2. Temperature dependence of the six rate constant ratios. Figure 2(c) includes a point fromDeMore(1992a).

Table 1. Ratios Measured and Their Temperature Dependence

Ratio	Arrhenius Expressiona	Ratio at 298 K
$k(CH_3CCl_3) / k(134a)$	(1.22 ± 0.17) exp ((219+ 44)/T)	2.54
$k(CH_4) / k(134a)$	(2.24 ± 0.78) exp((-82 ± 115)/T)	1.70
k(125) / k(134a)	(0.48 ± 0,12) exp ((12 ± 79)/T)	0,50
$k(CH_3CCl_3) / k(134)$	(0.84 ± O. 10) exp ((212 ± 37)/T)	1.71
k(134a) / k(134)	(0.85 ± 0.07) exp ((-80 ± 25)/T)	0.65
k(125) / k(134)	(0.48 ± O. 11) exp ((-109+_ 77)/T)	0.33

(a) Errors shown are standard deviations. Actual uncertainties are approximately a factor of 1.3 in the A-factor ratios and 75-125 K in the $\Delta E/R$ values.

Table 2. Derived Rate Constants for HFC- 134a and Comparison with Previous Recommendations.

k (134a)	k(298 K)	Reference Compound	Reference Rate Constant	Source
This work				
1.5×10^{-12} exp (-1769/T)	$3,9 \times 10^{-15}$	CH_3CCl_3	$1,8 \times 10^{-12}$exp(-1550/T)	JPL 92-20
1.3×10^{-12} exp (-1738/T)	3.8×10^{-15}	CH4	2.9 x 10-12exp (-1820/T)	JPL 92-20
1.2×10^{-12} exp (-1712/T)	3.8×10^{-15}	CF3CF2H	5.6 x 10-13 exp(-1 700/T)	JPL 92-20
JPL 92-20				
1.7×10^{-12} exp(-1750/T)	4.8×10^{-15}			
IUPAC				
8.4×10^{-13} exp(-1535/T)	4.9×10^{-15}			

Units are cm^3/molecule-s.

Table 3. Derived Rate Constants for HFC- 134 and Comparison with Previous Recommendations,

k (134)	k(298 K)	Reference Compound	Reference Rate Constant	Source
This work				
$2.1 \times 10^{-12} \exp(-1762/T)$	5.7×10^{-15}	CH_3CCl_3	$1.8 \times 10^{-12} \exp(-1550/T)$	JPL 92-20
$1.5 \times 10^{-12} \exp(-1660/T)$	5.7×10^{-15}	CF3CFH2	$1.3 \times 10^{-12} \exp(-1740/T)$	This work[a]
$1.2 \times 10^{-12} \exp(-1591/T)$	5.8×10^{-15}	CF_3CF_2H	$5.6 \times 10^{-13} \exp(-1700/T)$	JPL 92-20
JPL 92-20				
$8.7 \times 10^{-13} \exp(-1500/T)$	5.7×10^{-15}			
IUPAC				
-----------	5.7×10^{-15}			

Units are cm^3/molecule-s.

(a.) See Discussion Section.

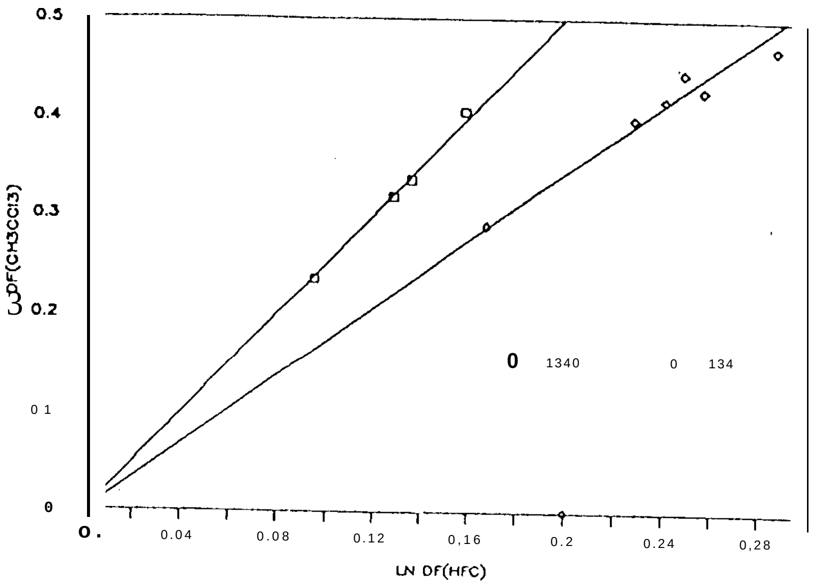

FIGURE I

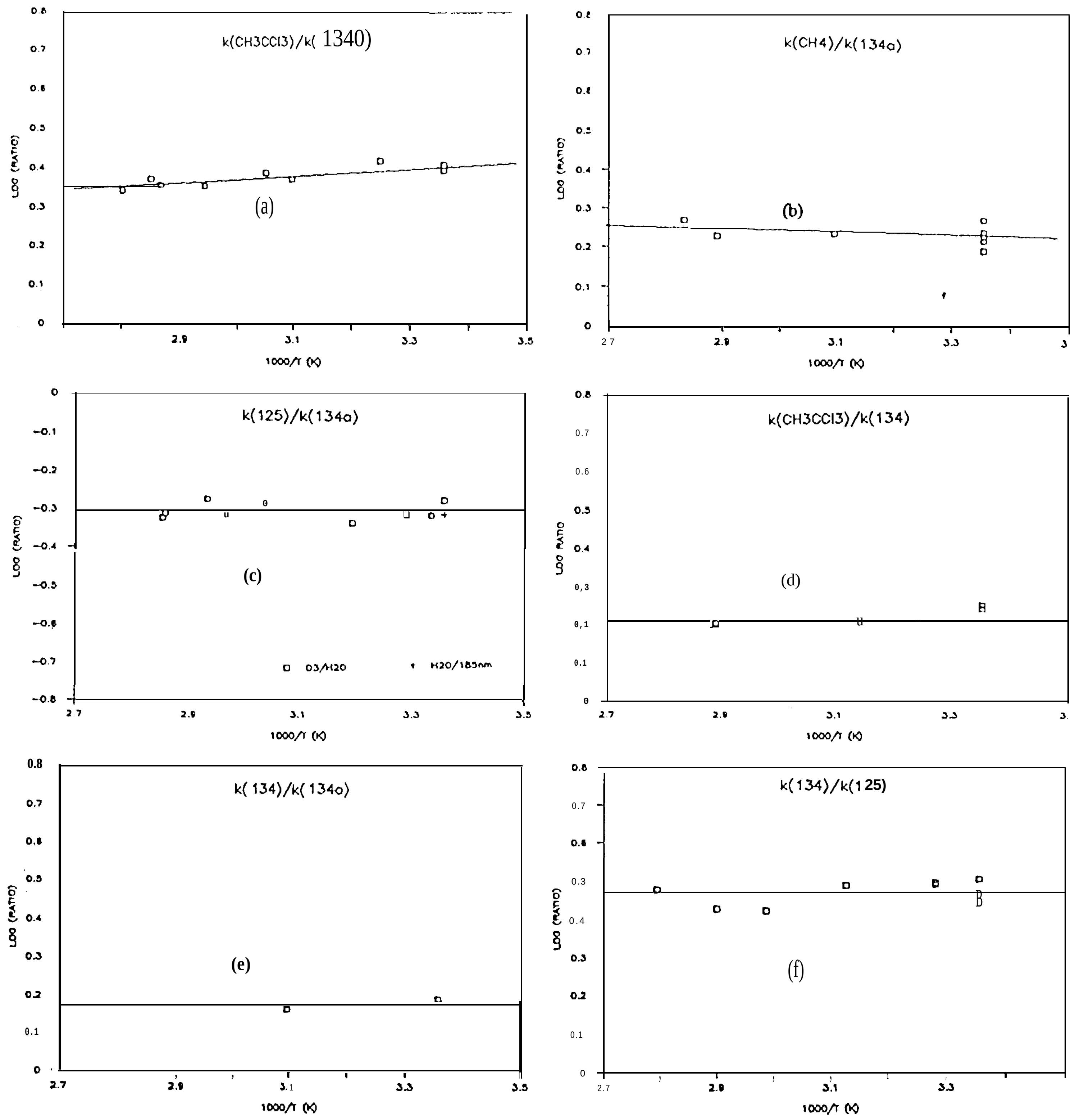
k(CH3CCl3)/k(1340)
(a)
k(CH4)/k(134a)
(b)
k(125)/k(134a)
(c)
O3/H20
H20/185nm
k(CH3CCl3)/k(134)
(d)
k(134)/k(134a)
(e)
k(134)/k(125)
(f)
LOG (RATIO)
1000/T (K)

FIGURE 7